The Pennsylvania State University

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Phase 1: Study of Second Phase Particles and Fe content in Zr Alloys Using the Advanced Photon Source at Argonne

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1. Introduction

During this funding period, we started the examination of Zr alloys using the microbeam facility at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). Two students were engaged to work on the project, and they performed the initial part of their graduate work , taking the required courses and starting on their thesis research. They have spent the summer of 1999 working at ANL, and will conduct further experiments in the APS in the beginning of the next funding period.

We conducted a trial run of Zircaloy specimens at the beam line operated by B.Lai, Z.Cai and co-workers. During this first experimental test of the idea of using the APS to study second phase particles in Zircaloy, we conducted both bulk diffraction and micro-diffraction studies principally of Zircaloy 4 and Zircaloy 2, (in over-aged condition).

The results show that (i) it is possible to detect and identify second phase particles using bulk diffraction at APS, and (ii) that it is also possible to interrogate individually the Zr matrix and second-phase precipitates using the microbeam facility at the SRI- CAT 2ID-D/E we utilized. Some experimental difficulties were also identified that will have to be addressed to obtain the information desired. Foremost among these is the issue of crystallographic texture (in relationship to making a quantitative determination of precipitate volume fraction) and of parasitic Fe counts from the equipment (which would affect the attempts to obtain information about the Fe in the matrix). Both problems are thought to be solvable. The indications are that the APS has great potential to give new and important information about the state of alloying elements in Zr alloys, whether in precipitates or in the matrix.

2. Bulk diffraction studies

We examined both Zircaloy 2 and Zircaloy 4 aged for 50h at 1055 K (782 C). Precipitates should be in the range of 0.1 to 0.5 μm after such heat treatment. The

objective of the examinations was to detect second phase particles, which have a small volume fraction in the Zr matrix. The examinations have to be performed in the 2θ region away from the Zr peaks, so the region between $10\bar{1}0$ and $10\bar{1}2$ is promising. Preliminary work showed that the Zr $(Cr, Fe)_2$ hcp and fcc precipitates have extra peaks in that region. The $Zr_2(Ni, Fe)$ precipitates unfortunately have their main peaks mostly close to Zr peaks so they will be harder to find. One of the typical measurements obtained is shown in figure 1 which shows a CCD picture of a diffraction pattern from Zircaloy 4. The $Zr(Cr.Fe)_2$ lines are indicated as well as those of the matrix Zr. The Zr peaks are very strong, and indicate a strong basal texture of the Zircaloy 4 sheet material, as expected. We rocked the sample during the experiment to obtain smoother rings. Extra peaks were seen and identified as hcp Zr $(Cr_{0.5}, Fe_{0.5})_2$ (card number 42-1289), hcp $MgZn_2$-type Laves phase; these peaks were $10\bar{1}3$, $20\bar{2}0$ and $11\bar{2}2$, representing all peaks that should have been seen for that phase in that region of reciprocal space. The respective peaks are indicated.

In Zircaloy 2 the same peaks for hcp Zr $(Cr, Fe)_2$ were seen, but also others that appear to be related to the cubic Zr $(Cr, Fe)_2$ phase. The Ni-based precipitates were not seen (this means one peak of reasonably low intensity which was not seen at 2θ=44.24 and one low intensity one at 39.2). This could be due to a smaller number of large Ni-based precipitates than of Cr-based precipitates, which happen to have the wrong orientation relationship to be observed near the basal orientations. This will be investigated further.

3. Microbeam Study of Precipitates in Zircaloy

Using the x-ray micro-focusing beam line at the APS devised by Yun et al.[1], we intend to study the chemical state of alloying elements such as Fe in the matrix of Zircaloy. The apparatus creates a micro-beam with diameter as small as 0.1 μm in diameter. This is a unique capability of this beam line which allows us to obtain detailed structural information with very high spatial resolution.

By translating the sample and recording the fluorescence yields for several elements at different locations, we constructed compositional maps of a 10 x 10 μm region in Zircaloy-2. The beam in this instance was 0.15 μm vertically and 0.2 μm horizontally; because of the angle the projected horizontal size of the beam is likely to have been ~0.4 μm. The fluorescence maps for Fe, Ni and Cr are shown below in figures 2-4. The Fe-Cr and Fe-Ni based precipitates can be clearly distinguished, showing that it is possible to place the beam in between the precipitates to obtain information on the matrix. Another possibility is to obtain either diffraction or chemical information on the precipitates themselves.

[1] 1 W.Yun, B.Lai, D.Shu, A.Khounsary, Z.Cai, J.Barraza and D.Legnini, "Design of a dedicated beam line for xray microfocusing and coherence-based techniques at the Advanced Photon Source", Review of Scientific Instruments 67 (9) 1996, 1-4.

In order to do this, however, we will have to diminish the background of Fe that was present when the sample was removed. These counts are likely from stainless steel in the equipment, and they diminished considerably when Al shielding was put around the detector (counts went from 7000 c/s to ~60 c/s). Still more will have to be done to detect the very low amounts of Fe from the matrix.

Another problem appeared in the specimen translator drives (which exhibited some drift), so that the position of the beam could not be determined with as much precision as would be expected. The cause of the drift was not immediately determined, but it is likely to have been related to the motor drive of the specimen translators. The translator drives have now been replaced by more precise models, so this is not expected to be a problem.

TEM samples, because of their small thickness may be ideally suited for this type of study. The use of TEM samples would reduce the activity to be handled when examining irradiated samples, and would address the problem of "buried precipitates", i.e. thinking we are getting information from the matrix by pointing the beam in-between precipitates we might be getting information from precipitates just under the surface. Some preliminary calculations indicate that this may be a manageable problem, as for the beam energies of interest we expect only a few % probability that a "buried precipitate" would be excited by the microbeam.